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Diffuse CO_2 emission at Sfânta Ana lake-filled crater (Eastern Carpathians, Romania)

Nicolae Frunzeti*, Călin Baciu

Babeş-Bolyai University, Faculty of Environmental Science and Engineering, Cluj-Napoca, RO-400294, Romania

Abstract

In the framework of studies on gas emissions, the surface and time distribution of carbon dioxide flux represent an important geochemical tool for volcanic activity monitoring. Ciomadu volcano, located on the southern part of Eastern Carpathians, witnesses the most recent eruption in the whole Carpathian range. In order to understand the actual behavior and to assess the present phase of this extinct volcano, the diffuse CO_2 flux near Sfânta Ana Lake was measured using the closed chamber method. Carbon dioxide flux values ranged from about 2 g m^{-2} day^{-1} up to 90 g m^{-2} day^{-1}. The measurements were performed in different places by respect to the Sfânta Ana crater. The results show a tendency of increase in carbon dioxide flux starting from the flank toward the crater, with the highest values located close to the shore lake. A carbon dioxide flux distribution map for the measurements inside the crater was produced, that reveals a particular pattern distribution of CO_2 flux.

Keywords: CO_2 flux; volcanic activity; Ciomadu volcano; Eastern Carpathians; Romania.

1. Introduction

In the last two decades, numerous studies have focused on diffuse carbon dioxide emission released from volcanoes [1, 2, 3, 4] and geothermal areas [5, 6]. It has been recognized that diffuse degassing may have a much important role in the amount of released gas, larger than from the gas released from the crater [1, 2]. But this is not generally applied in all volcanoes as no evidence of diffuse emission of volcanic carbon dioxide was observed at Popocatepetl volcano [7]. Carbon dioxide is released from the soil in most of the terrestrial environments as a result of roots respiration and decomposition of organic

* Corresponding author. Tel.: +40-264-307030; fax: +40-264-307032
E-mail address: frunzeti.nicolae@ubbcluj.ro

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matter. In temperate climate the average values of carbon dioxide flux from biogenic sources are about 3 g m^{-2} day^{-1} [8, 9, 10]. However, the carbon dioxide may have a different source due to endogenous processes like thermal degradation of carbonates, metamorphism and oxidation of ancient organic carbon in sedimentary rocks [11], magma or mantle degassing in tectonic regions [12] that can migrate to the surface through preferential pathways like faults or fractures [13]. In most of the cases, the geogenic degassing is much more intensive than the emissions generated by the biotic processes.

The spatial and time distribution of diffuse carbon dioxide emission has become a widely used geochemical tool for volcanic [14, 15] and geothermal [6] activity monitoring. The emission rate of diffuse CO_2 emission can increase greatly before a volcanic eruption [16]. The upward migration of carbon dioxide is facilitated and controlled by active faults and the occurrence of high emission of carbon dioxide may represent a good indicator to identify the location and the direction of the fault systems [17].

Diffuse emission of carbon dioxide represents an important indicator of the actual status of the volcanic and geothermal phenomena [16, 18]. Even if it represents an important source of C in the atmospheric budget, it seems to be strongly underestimated. Very few surveys have been carried out at volcanoes with weak or non-existent plume emission from summit crater [3, 4].

Consequently to the explosive Quaternary volcanism of Ciomadu volcano, two craters are still visible, one of them hosting Sfânta Ana Lake which represents the main area of the present work. The twin crater of Sfânta Ana is Mohoş that host a peat bog. The released gas close to Sfânta Ana Lake consists of CO_2 (97.69% vol) followed by nitrogen, methane, oxygen, argon and helium [19]. The origin of He deduced from high $^3He/^4He$ ratio of 3.16 R_m/R_a, [19] or 4.16 [20] (where R_m is the measured value and R_a is the air value) indicates that about 50% of the total He is mantle derived. Seismic tomography shows a lower velocity zone, suggesting weaker and hotter mantle beneath the southeastern corner of the Transylvanian Depression.

The main goal of this work is to study the spatial distribution of diffuse carbon dioxide emission and its relation to the level of volcanic activity in one of the two craters of the extinct Ciomadu volcano. This work presents the first results of a large project focused on the estimation of diffuse carbon dioxide emission, carried out in October 2011 around Sfânta Ana Lake-filled crater.

2. The geographical and geological setting

The study area is located in the South Harghita Mountains, part of the Neogene-Quaternary volcanic range, in the Eastern Carpathians, and represents the southern limit of the Carpathian calc-alkaline segment (Călimani-Gurghiu-Harghita volcanic chain). Ciomadu volcano consists of a large number of lava domes (Fig. 1) located in the central part of the edifice (Ciomadu Mare, Ciomadu Mic, Komlósárok, Haramul Mare, Köves Ponk), and the oldest domes isolated farther to the east (Bálványos, Puturosul, Muntele Mare, Haramul Mic) [21]. The central dome hosts two craters resulted from two explosives eruptions: Sfânta Ana and Mohoş. The dacitic explosive-extrusive volcanism in the Ciomadu massif developed on a basement represented by the Cretaceous flysch and by older Pliocene pyroxene andesites [22].

The activity of Ciomadu volcano started about 1 Ma BP, with the Bálványos dome extrusion from the eastern part of the volcano. The volcanic activities continued for the next 0.5 Ma in the same non-violent phase which leads to the complex built-up of the volcano edifice. In the last few hundreds of ka, the volcanic activity became strongly explosive. This phase is characterized by two strong explosive eruptions which lead to the formation of two craters: Sfânta Ana and Mohoş. The last eruption of Ciomadu volcano is less than 50 ka in age, but the date is still under debate somewhere between 10,700 years [23] and 42,650 years BP [24]. The youngest age is confirmed also by the multi-proxy investigation carried out on the sediments from the bottom of the lake which report the age of the lake of about 9,800 years [25].

The area is abundant in post-volcanic features like mineral water springs, mofettes, with abundant flow of carbon dioxide. A strong smell of hydrogen sulfide may be observed especially in the eastern part of the volcano in a lava dome named Muntele Puturosul (The Stinky Mountain) with large amount of discharged carbon dioxide.

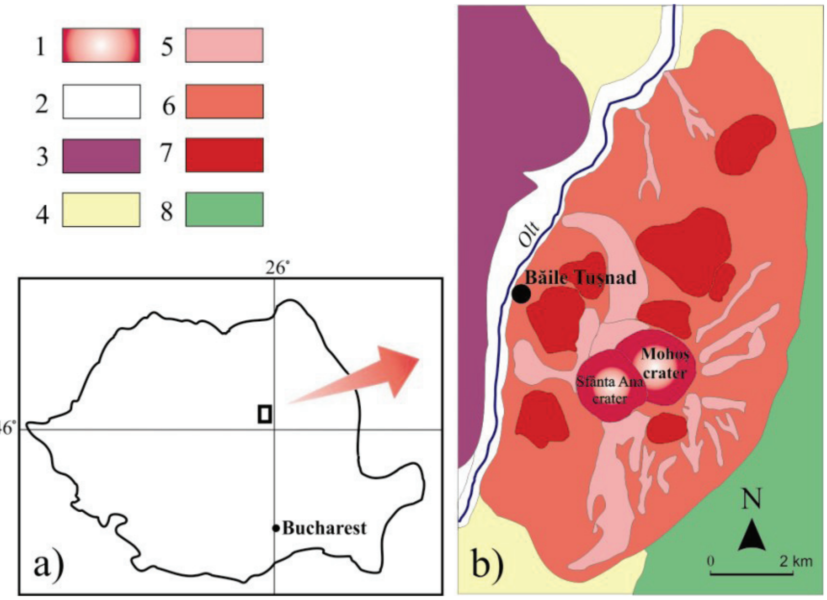

Fig. 1. a) The map of Romania with the study area, b) The geological map of Ciomadu volcano (redraw after [24]) 1) crater, 2) Holocene alluvial deposits, 3) Pilişca volcano, 4) Pleistocene sedimentary deposits, 5) pyroclastic flow surface, 6) pyroclastic rocks, 7) lava domes, 8) Cretacic flysch

Some mineral water springs with anomalous high temperature occur near Băile Tuşnad in the western part of the volcano. In the late seventies, two deep wells were drilled to confirm the thermal anomalies. The highest recorded temperature was 78ºC at 1140 m depth. The source rock was found to be a volcanic intrusion beneath the folded flysch basement, intercepted at a depth of 400-700 m [26]. Ciomadu volcano, along with the whole Harghita Mountains hosts the strongest heat-flow anomaly in Romania of 80-120 mW m^{-2} [27].

Sfânta Ana Lake is located 3 km south-east of Băile Tuşnad at 950 m asl. It has an approximately circular shape with the perimeter of about 1.7 km and the largest diameter of 650 m. The area of the lake is 0.193 km^2 and the deepest measured point of about 7 m [28].

No gas flux measurements were performed at Ciomadu volcano and this work represents the first survey of carbon dioxide flux which may represent an important tool to understand the actual phase of this extinct volcano.

3. Material and methods

Carbon dioxide fluxes were performed in October 2011 by using the closed chamber method, the same technique that was used in many other places with diffuse emission (e.g. [3, 4]). A portable diffuse flux meter (West System srl, Italy) equipped with CO_2 sensor, and wireless data communication to a palm-top computer was used. If the rate of increase of gas concentration in the chamber is constant, linear regression can be used to calculate the gas flux (F) by the equation [29]:

$$F = (Vc / Ac) \times [(c_2 - c_1) / (t_2 - t_1)] \quad [g\ m^{-2}\ day^{-1}]$$

where Vc (m^3) is the volume of the chamber, Ac (m^2) is the footprint area of the chamber, c_1 and c_2 (mg m^{-3}) are gas concentrations at time t_1 and t_2 respectively (days).

The CO_2 detector is a double beam infrared sensor (LI-COR) with a range of 0 to 20 000 ppmv. The device includes also the methane sensor which is composed by semiconductor (range 0-2000 ppmv, detection limit 1 ppmv, resolution 1 ppmv), catalytic (range 2000 ppmv – 3% v/v) and thermal conductivity (range 3-100% v/v) detectors.

A total number of 71 carbon dioxide flux measurements were performed. Thirty four measurements were distributed in tandems (the first measurement of each tandem located at 3 m from the edge of the lake, and the second at 30 m) at a distance of about 100 m between them. Other 15 measurements were distributed at different distance from the lake shore to observe if any anomalous emissions could be found. The Surfer software was used to produce the map of flux distribution of carbon dioxide for the measurements inside the crater. A 2.3 km long transect, starting from the South-Eastern part of the lake was set and the flux was measured every about 100 meters (excepting the first two measurements which were located at 3 and 30 m distance from the lake shore).

4. Results and discussion

The diffuse carbon dioxide flux ranged from 2.4 g m^{-2} day^{-1} to 87.9 g m^{-2} day^{-1}, and no methane flux above the detection limit of the used method was found. The maximum CO_2 flux was recorded at 3 m distance from the southern shore of the lake.

The transect shows a tendency of increase of the carbon dioxide flux starting from the most distant measurement point to the proximal points by respect to the lake (Fig. 2b). The lowest values of carbon dioxide flux of about 2 g m^{-2} day^{-1} were measured at the most distant points (2.3 and 2.2 km from the lake shore) followed by a relatively constant increase for the next 1 km up to 9.7 g m^{-2} day^{-1}. Then the carbon dioxide flux remains constant around the value of 9 g m^{-2} day^{-1} until a distance of 0.2 km from the Sfânta Ana Lake shore. The highest values on the transect were 37.3 g m^{-2} day^{-1} and 49.5 g m^{-2} day^{-1} located at 0.03 km and 0.003 km respectively from the shore of the lake.

The spatial distribution of carbon dioxide flux drawn by Surfer Software by using the Kriging interpolation method indicates an anomalous emission around the lake, with the highest values located in the south, east and west, but slightly above normal values to the north (Fig. 3b). The surface of Sfânta Ana Lake was not included in the interpolation as no measurements were performed on the surface of the lake.

As it may be observed in Table 1, the highest mean value recorded of carbon dioxide flux was located around the lake. The proximal two measuring points of the transect were included in the diagram of the Fig. 2 but not included in the Table 1 as measurements on the transect, consequently they were considered as the measurements around the lake.

Table 1. Statistics of carbon dioxide flux measurements

Location	Number of meas.	Min (g m^{-2} day^{-1})	Max (g m^{-2} day^{-1})	Mean (g m^{-2} day^{-1})	Standard deviation	Standard error
Transect*	22	2.3	13.9	6.5	2.2	0.11
Around the lake	34	6.3	87.9	29.3	13.7	0.14
Inside the crater	15	4.5	15.8	7.6	2.04	0.02

*the proximal two measuring points of the transect not included

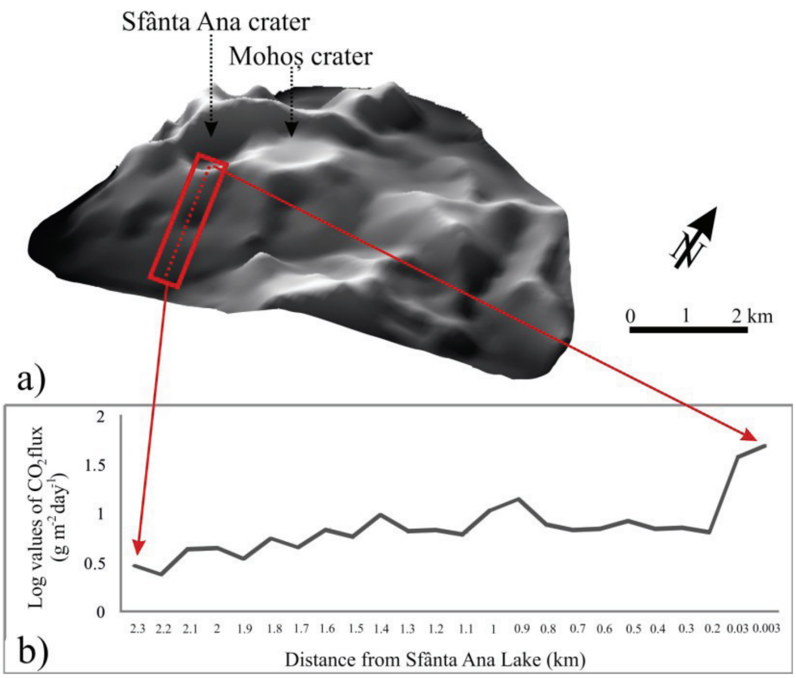

Fig. 2. a) Overview of Ciomadu volcano; b) Logarithmic values of CO_2 flux on the transect

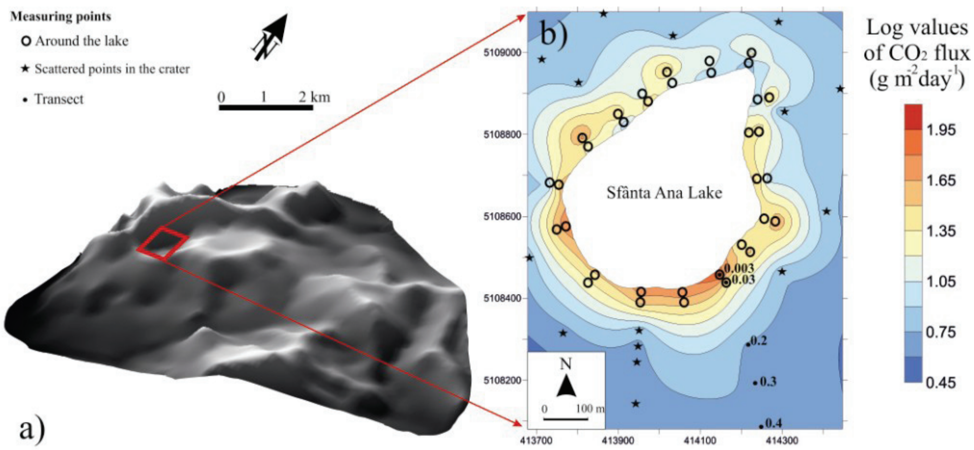

Fig. 3. a) Overview of Ciomadu volcano; b) The CO_2 flux distribution at Sfânta Ana Lake

The highest values were measured inside the crater with no significantly high values outside the crater, although an increase tendency was observed as we approached the shore of the lake. This indicates that certain amount of carbon dioxide is still degassing from different depths. Similar results regarding the CO_2 emission inside craters for the extinct volcanoes are reported in the literature [4].

5. Conclusion

Very few studies had been carried out regarding the composition and origin of gas but no measurements of carbon dioxide flux were performed at Ciomadu volcano.

This work represents the first survey of the carbon dioxide flux, carried out in October 2011 inside the Sfânta Ana crater, around the lake and on the flank. The flux measurements indicate that carbon dioxide is increasing as we approach the crater with an anomalous degassing occurring very close to the shore of Sfânta Ana Lake. The maximum values which are above the values from biogenic processes suggest that the extra carbon dioxide may have an endogenous source. But the overall results show a relatively low flux of carbon dioxide which indicates that the volcanic system of Ciomadu volcano is in a phase of quiescence. Further measurements need to be performed in a larger area and in different periods of time to observe if there is any fluctuation or different pattern on flux distribution.

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